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Toxicity testing of combustion products of polyurethane and polyvinylchloride

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Achtergrond

In het kader van de A-opdracht 'pyrolyse' is de afgelopen drie jaar gewerkt aan het ontwikkelen van een standaardtest waarmee de giftigheid van verbrandingsproducten van kunststoffen en diverse soorten kruit kan worden vastgesteld. De voornaamste drijfveren voor dit onderzoek worden onderstaand genoemd.

- De laatste decennia is er sprake van sterk toenemende toepassing van uiteenlopende soorten kunststof in ondermeer de bouw, scheepsbouw en voertuigconstructie. Deze toename lijkt in de pas te lopen met het stijgend percentage van (dodelijke) slachtoffers tijdens brand dat te wijten is aan inhalatie van (giftige) rookmengsels, eerder dan aan de brand zelf.
- Men realiseert zich binnen defensie dat de kwetsbaarheid van personeel vergroot is door toenemende toepassing van brandbare kunststoffen op militair materieel (schepen, vliegtuigen, voertuigen).
- Er is behoefte aan een objectieve vergelijkende test waarmee toe te passen materialen kunnen worden vergeleken.
- Er is, in algemenere zin, behoefte aan kennisopbouw op dit gebied, zodat nauwverwante specifieke vraagstukken op geïntegreerde wijze benaderd kunnen worden. Voorbeelden hiervan zijn:
 - vergelijking van de giftigheid van camouflagerookartikelen (bijvoorbeeld HC-rook) [Busker en Kuijpers, 1996a] en van gekleurde rookartikelen;
 - onderzoek naar schadelijke effecten van kruitdamp [Busker et al., 1996b];
 - opstellen van richtlijnen op NATO-niveau (STANAG) voor onderzoek naar toxiciteit van rook.

In eerdere rapporten [Busker et al., 1994 en 1997] is reeds beschreven welke eisen aan een dergelijke test moeten worden gesteld en is de eerste opzet van de test geïllustreerd aan de hand van een serie proeven. In dit rapport ligt de nadruk op de verbeteringen en op de validatie van de toxiciteitstest. De validatie van de test is uitgevoerd aan de hand van het vaststellen van de giftigheid van een tweetal veel gebruikte kunststoffen, polyurethaan (PUR) en polyvinylchloride (PVC). Ter

validatie is gekozen voor de volgende aanpak, waarbij beoogd is aan te tonen dat de test geschikt is voor het beantwoorden van een diversiteit aan inhoudelijke, c.q., praktische vragen.

- 1 Kan met gebruikmaking van de test de giftigheid van verschillende verwerkingsvormen van een bepaald type kunststof worden vergeleken?
- 2 Is de test geschikt voor uiteenlopende verbrandingscondities (temperatuur, zuurstofgehalte enz.)?
- 3 Kunnen verschillende soorten kunststof met een voldoende groot onderscheidend vermogen worden bestudeerd?
- 4 Is de test geschikt om vergelijking met literatuurgegevens uit te voeren?

Uitgevoerde werkzaamheden en resultaten

In de testopstelling worden hoeveelheden van 2-100 gram plastic verbrand. Ratten worden gedurende 30 min blootgesteld aan het complete rookmengsel. Behalve de overleving, werden ook subletale effecten zoals ademhalingsdepressie en longbeschadiging bestudeerd.

Uit de experimenten blijkt dat de giftigheid van verbrand PUR-flexibele plaat groter is dan die van PUR-schuim. Dieren die waren blootgesteld aan de verbrandingsproducten van PUR gingen tijdens of kort na de blootstelling dood. Bij de PUR-proeven werden concentraties koolmonoxide (CO) gemeten die in de buurt van de letale concentratie lagen. Kennelijk is CO het belangrijkste toxische product dat bij PUR gevormd wordt. Verder werden bij PUR-schuim ook toxische hoeveelheden van het zeer giftige blauwzuur (HCN) gevonden.

Bij vermindering van het zuurstofgehalte tijdens de verbranding (smeulen) nam de overall toxiciteit niet toe. Echter, de CO-concentratie was aanzienlijk geringer, plusminus eenderde van de letale concentratie. Daarentegen was de HCN concentratie aanzienlijk toegenomen tot plusminus 66% van de letale concentratie.

Bij verbranding van polyvinylchloride (PVC) speelt naast de vorming van CO ook zoutzuur (HCl) een belangrijke rol. Opvallend is dat de toxische effecten veel trager tot stand kwamen dan bij de PUR-experimenten.

Bij vermindering van het zuurstofgehalte tijdens de verbranding van PVC nam de toxiciteit niet toe. Op grond van de vastgestelde toxiciteit moet geconcludeerd worden dat andere stoffen dan CO en HCl een belangrijke rol spelen.

De met deze test gevonden toxiciteitsindices zijn binnen zekere grenzen goed vergelijkbaar met literatuurwaarden. Vergelijking blijft niettemin moeilijk, gezien de verschillen in herkomst van de materialen, herkomst van de proefdieren en experimentele details. Daarom ligt de kracht van dit type toxiciteitstesten in de rechtstreekse vergelijking van te onderzoeken materialen. Qua opzet en uitvoering is de test vergelijkbaar met de zogenaamd 'Pittsburgh University' methode.

Conclusie

Het voorafgaande onderzoek heeft geresulteerd in een gevalideerde test. De test heeft onder meer toepassing gevonden in een vergelijking van pijpisolatiematerialen ten behoeve van DMKM (Afdeling Scheepsbouw) en een vergelijking van de verbrandingsproducten van diverse kruitsoorten ten behoeve van DMKL (Afdeling Munitie). Momenteel is de test beschikbaar voor specifieke vraagstellingen vanuit de krijgsmachtdelen.

Contents

	Managementuittreksel	2
1	Introduction	6
2	Materials and methods	9
	2.1 Materials	9
	2.2 Animals	9
	2.3 Experimental set-up	9
	2.4 Combustion	9
	2.5 Animal handling	10
	2.6 Lung function measurement	11
	2.7 Biochemical markers	11
	2.8 Histo-pathology	11
3	Results	13
	3.1 Combustion of polyurethane (PUR)	14
	3.2 Combustion of PVC	19
4	Discussion	23
5	References	26
6	Authentication	30
	Annex:	
	A Oven and animal exposure unit	

1 Introduction

The continuous increase in application of plastics by modern industry and for construction yields problems with regard to fire safety. The percentage of fatal accidents in fires due to inhalation of toxic combustion products outnumbers that due to the deleterious effects of heat or of the fire itself. Over the last decades, the percentage of inhalation fatalities has increased to 80% [Berl and Harpin, 1979; Herndon et al., 1987]. Disasters involving fire repeatedly emphasise the need for better insight into the danger of smoke inhalation [Kinsella et al., 1988]. This was recently illustrated by the 1996 Düsseldorf fire, in which PVC exposure was claimed to be the main cause of injury.

Health problems caused by smoke inhalation during fires have special military interest. Notably the Navy is faced with the problem in war vessels, which are equipped with huge amounts of insulation materials. During the Falklands war, this was illustrated dramatically by the missile attacks on H.M.S. Sheffield and the troop-carrying ship Sir Galahad [Williams et al., 1983]. More people suffered from the inhalation of toxic gases released from burning plastics, than from the hit of the missile itself or from the resulting flames or heat of the fire.

In cases of fire casualties, it is rarely known which combustion products contribute to the overall toxicity. Usually, carbon monoxide (CO) is the most important factor. However, especially in the case of burning plastics, the contribution of other pyrolysis products can be considerable. These include well-known compounds such as hydrogen cyanide (HCN), nitrogen oxides (NO₂, NO) and aldehydes [Sasse et al., 1988]. Also small amounts of unknown highly toxic substances may contribute to the overall toxicity [Arito and Soda, 1977]. Formation of such compounds, even in small-scale fires with moderate total emission, may result in a considerable toxic burden.

A research project was initiated by the Dutch Ministry of Defence to develop a method for testing the combustion toxicology of given products. Over the last decades, methods to study the toxicity of complex mixtures by making use of literature toxicity data of a number of the individual components have substantially improved. The N-gas model has gained recognition [Gad and Anderson, 1990]. Nevertheless, these methods suffer from the uncertainty as to the contribution of minor toxic products to the overall toxicity, the origin and reliability of toxicity data and the involvement of synergetic toxicity. Therefore most accepted methods use experimental thermolysis combined with exposure of experimental animals to the smoke mixture. Several fire models have been selected by ISO TC92/SC3, including the University of Pittsburgh [Alarie and Anderson, 1981], NBS (=NIST) [Gad and Anderson, 1990; Levin et al., 1982] and DIN 53436 [Prager, 1988] methods.

It was decided to develop a full toxicological test, in close agreement with accepted methods described in the literature. This model should assist in questions regarding the safety of potentially applied materials from a combustion-toxicological point of view. The main strength of such a test is that it allows direct comparison of several

materials or experimental conditions. With respect to the combustion conditions, several criteria should be met. The combustion temperature should be high enough to decompose all samples being tested; it should not be higher than that of average developing fires (800 °C). Sufficient oxygen should be present to mimic open-space fires; on the other hand it should be possible to vary the oxygen content to mimic closed-space fires (pyrolysis conditions) [Alarie, 1985]. Furthermore, it should be applicable to investigate the usefulness of possible medical intervention. Although the emphasis is mostly on lethality as such, it should also consider non-lethal (ir)reversible damage to the lungs. Effects of smoke on breathing may induce considerable hindrance to rescue efforts.

An earlier report [Busker et al., 1994] described the first phase of this project, which was aimed at the development of the combustion toxicology model. In that phase, emphasis was on technological aspects, and on the effect of combustion temperature on product formation as well as the resulting toxicity. In the development phase, attention was paid to resemblance of the fire conditions to real fires. This motivated the choice for a dynamic flow system and the use of a tube furnace oven [Edgerly et al., 1982]. Using a single model plastic, polyurethane (PUR) flexible plates, it was demonstrated that the model yields data that are in accordance with literature data. With that model, which was still under development then, it could be demonstrated that the toxic effects of the combustion gases of PUR are mainly due to emission of carbon monoxide (CO). In addition, the effect of combustion temperature on toxicity was investigated.

Limitations of the method at that stage were:

- the necessity to filter the combustion mixture; it was not possible to expose the animals to the complete smoke mixture;
- the limited capacity of the tube furnace oven; several combustions with small amounts of sample had to be performed to generate sufficiently toxic levels of combustion gases;
- the absence of histo-pathologic evaluation of the effects of the toxic substances;
- the limited flexibility with regard to the combustion conditions.

The second stage of model development was therefore aimed at altering of the animal exposure unit to allow inhalation of solid particles; purchase and installation of a of larger capacity oven; expansion of the number and scope of the toxicological end-points.

Furthermore, the combustion toxicology model as such had to be validated on the basis of the practical research demands. It is important that the influence of practical variables such as the type of polymer used in the plastic, the type of plastic with regard to application and the oxygen concentration on toxicity can be investigated. For that reason, the following experimental design was used to follow the process of validation:

- comparison of the combustion toxicology of PUR in the form of a flexible plate with that of rigid foam PUR;

- comparison of atmospheric conditions with oxygen-deprived conditions, using both PUR and polyvinylchloride (PVC); fires with O₂ concentration of 5% or less are called non-flaming or pyrolytic [Hartzell, 1991];
- direct comparison of the combustion toxicology of two different plastics, PUR and PVC;
- perform experiments that allow comparison with literature data.

2 Materials and methods

2.1 Materials

Samples of flexible polyurethane 4513 were kindly donated by Bayer, Leverkusen, Germany. The plates were cut into strips of 1x1 cm (with the length required to obtain the desired weight), weighing 1.5 g/cm. A 1 m³ block of PUR foam was donated by BASF; it was sawn into 4x4 cm bars of the desired length. PUR samples were of the toluene di-isocyanate type (TDI). PVC used as construction material was purchased (Quantum) and sawn into 0.5x1 cm bars of desired size.

2.2 Animals

Male Wistar WU rats (weight: 200-300 g; age: 10-14 weeks) from Charles River (Sulzfeld, Germany) were used. The animals, arriving at least 8 days before the experiment, were kept at a 12:12 h light-dark cycle (humidity: 50-70%; temperature 24°C) having free access to food and water before and after the experiments.

2.3 Experimental set-up

For the questions to be answered, five series of experiments were performed. In total, two different plastics were used: PUR and PVC. Two different conditions were tested: atmospheric (20% oxygen) and ~100% nitrogen (see below). Two product formulations were compared: PUR flexible plate and PUR rigid foam. Each series consisted of 5-8 separate experiments with differing amounts of sample. The number of experiments within a series depended on the number of surviving animals. In each case, sufficient experiments were performed to obtain enough surviving animals for histology and biochemistry. In each of the experiments, six rats were exposed, while two rats served as unexposed controls.

2.4 Combustion

The samples (2-15 g) were combusted in a Heraeus tube furnace oven RO 7/75, supplied with a control unit Thermikon P type RE 2.1. For a detailed photograph see Annex A. The oven is equipped with a specially designed quartz tube (120 cm, i.d. 45 mm), which is horizontally centred inside the heated part of the oven. Samples were placed in a glass tube, in-line connected with the quartz tube, together making up a closed system, to be placed into the quartz tube at the start of combustion. The oven was preheated to 800 °C (the maximal temperature reached in

average developing fires), and this temperature, registered using a Ni/Cr thermocouple, was maintained throughout the combustion. The air (or pure nitrogen) flow, delivered by a HiTec mass flow controller (Bronkhorst, Ruurlo, The Netherlands; #3 in Annex A) went through the quartz tube (2 l/min). It was diluted with a second airflow (8 L/min; #9 in Annex A) entering behind the oven. The airflow was checked using a Gilibrator flow calibrator (Meyvis, Bergen op Zoom, The Netherlands). The combined airflow, spontaneously cooled to $<50^{\circ}\text{C}$ was led into a animal exposure unit (Jaeger, USA; #7 in Annex A). This unit consists of a central cylindrical space, which has 9 radially situated outlets. Each outlet, a 3 cm long 1x1 cm stainless steel block with a cylindrical hole, serves to generate the smoke straight into the end of connected Battelle tubes. In this way the animals are forced to inhale the aerosol directly into the nose. The excess of flow leaves the apparatus by centrally placed tubing. The temperature of the smoke mixture was registered upon entering the animal exposure unit (#2 in Annex A), as well as at the location of the animals' noses (#8 in Annex A).

In the experiments performed with reduced oxygen concentrations, the quartz tube was flushed with nitrogen (2 l/min) for 10 minutes prior to combustion. During combustion, the primary 2 l/min nitrogen flow was maintained. An 8 l/min airflow was maintained for dilution and re-establishing close to normal oxygen (16-18% O_2) concentration at the level of the rats.

During the combustion, part of the smoke mixture was collected by means of sampling through a P3 filter (Gilair 5 sampling pump at 1 l/min). The filtered gas mixture was collected into a 50 l TedlarR (polyvinylfluoride) gas-sampling bag. This was used for the determination of CO, CO_2 , HCN, HCl, NO_2 , and aldehydes. After cooling, the unburnt material and the P3 filter were weighed.

2.5 Animal handling

Rats were weighed on the day of the experiment. Half an hour prior to exposure to combustion products, a pre-exposure lung function measurement was performed [Bergers et al., 1995]. In each experiment, six rats were exposed to the tested smoke mixture and two rats were used as unexposed controls. Five minutes after exposure, a second lung function measurement was performed for 10 minutes. Thereafter, 0.5 ml blood samples were drawn from the tail vein, and kept for subsequent analysis of blood hemoglobin. Thereafter, rectal body temperature was measured. The rats were then returned to their cages, and 14 days survival was scored.

On day 14 following exposure, half the number of the surviving animals were anaesthetised, the lungs were isolated and weighed (wet lung weight) and bronchoalveolar lavage (BAL) was performed. The lavage fluid was kept for subsequent determination of lactate dehydrogenase. Lung tissue samples were kept for determination of glucose-6-phosphate dehydrogenase and lung fibrosis. The lung tissues were homogenised in 10 vol. of a buffer containing 0.25 g NaEDTA and 9 g NaCl per l water. Lung homogenates (LH) and BALF were stored at -70°C .

The remaining (surviving) animals were sacrificed on day 14 for standard histopathologic evaluation.

2.6 Lung function measurement

Respiratory frequency and respiratory minute volume were determined by placing the animals in Battelle tubes connected to measuring chambers supplied with differential pressure transducers [Bergers et al., 1995]. Both measurements before and after exposure lasted 10 minutes.

2.7 Biochemical markers

To monitor exposure to CO, carboxyhaemoglobin (COHb) levels in blood were determined using an IL-282 CO-Oximeter (Instrumentation Laboratory, IJsselstein, The Netherlands) which had been calibrated for rat blood.

Three markers were used to recognise pulmonary protein exsudation, an indication of lung oedema. Total protein levels in BALF were determined by the Bio-Rad method (Bio-Rad Laboratories, Veenendaal, The Netherlands). BAL-peroxidase activity was determined with guaiacol and peroxide as reagents [Bergmeyer, 1970] and with horseradish peroxidase (Sigma) as a standard. Lactate dehydrogenase (LDH) was assessed via depletion of NADH during incubation with pyruvate [Bergmeyer, 1970].

Total non-protein thiols in LH were determined according to Beutler et al. [1963]; glutathione was used as a reference. The activity of glucose-6-phosphate dehydrogenase (G6PD) in LH was determined spectrophotometrically by measuring the formation of NADPH [Bergmeyer, 1970] with purified G6PD from Sigma as reference. Total LH protein was measured as described above.

2.8 Histo-pathology

Animals were sacrificed 14 days after exposure for histopathological examination of the lung tissue and epithelial tissue of the nostrils. Rats were euthanized by i.p. injection with Nembutal (240 mg/kg).

2.8.1 Lungs

The lungs and trachea were uncovered and excised from the thorax. For fixation purposes, a 4% paraformaldehyde/PBS solution was perfused into the inflated lung through a tracheal cannula. A ligature was placed around the trachea; this kept the fixation solution from leaking out. Lungs and trachea were immersed in the same fixative for a period of at least 48 hours at room temperature.

After fixation, a 2 to 3 mm thick lung slice was cut longitudinally from a lobe of the lung. Infiltration with paraffin was performed in a Vacuum Infiltration Proces-

sor. The infiltrated lung slice was oriented in a base mould, embedded in paraffin and cooled to solidify. Three-micrometer sections of the lung slice were cut using a Jung microtome. The sections were stretched in a water bath and caught on glass slides. After drying, the slides were stained with Haematoxylin-Eosin. An external pathologist performed the histopathological examination.

2.8.2 Epithelial tissue of the nostrils

The lower jaw of the mouth was removed and the part of the head that contained the epithelium of the nostrils was immersed in a 4% paraformaldehyde/PBS solution for a period of at least 48 hours. After fixation, the bone tissue surrounding the nostrils was decalcified by a 1:1 solution of 53% formic acid and 8% sodium hydroxide, followed by the paraffin embedding procedure. Two to 3 mm thick transverse slices were cut ventral, central and caudal. Infiltration with paraffin was performed in a Vacuum Infiltration Processor. The infiltrated nostrils were oriented in a base mould, embedded in paraffin and cooled to solidify. Three-micrometer thick sections were cut using a Jung microtome. The sections were stretched in a water bath and caught on glass slides. After drying, the slides were stained with Haematoxylin-Eosin. An external pathologist performed the histopathological examination.

3 Results

Compared with the experiments described in an earlier report [Busker et al., 1994], an oven with a larger capacity was used. With this equipment even plastics of very low density, like PUR foam, can be easily investigated with a sufficiently high sample-weight (20 g, volume approximately 1 l). Also samples of higher density, up to 100 g, can be burned. Due to the construction principle of the Jaeger animal inhalation unit, rodents can be exposed to complete smoke mixtures.

Table 1: Lethality data obtained after exposure of rats to combustion products of several plastics. LD₅₀ was calculated from the amounts of plastic in grams, which were burnt in series of experiments (4-6 for each plastic). LC₅₀ was calculated from the amount in grams of burnt plastic divided by the total gas volume generated during the 15 minute exposures.

Experiment code	Plastic type	Conditions used	LD ₅₀ (g)	SEM (g)	LC ₅₀ (g/m ³)	SEM (%)	LCt ₅₀ (g.min/m ³)
PU foam	Polyurethane rigid foam (solid)	Atmospheric	13.3	0.94	89	6.3	1335 **
PU plate	Polyurethane flexible plate	Atmospheric	5.0	0.53	33	3.5	495
PU N-plate	Polyurethane flexible plate	100% nitrogen	5.5	0.49	37	3.3	555
PVC	Polyvinylchloride hard plate	Atmospheric	6.5	0.94	43	4.3	645 *
PVC N	Polyvinylchloride hard plate	100% nitrogen	3.9	0.40	26	2.6	390

* Signal different from PVC-N.

** Signal different from PU plate.

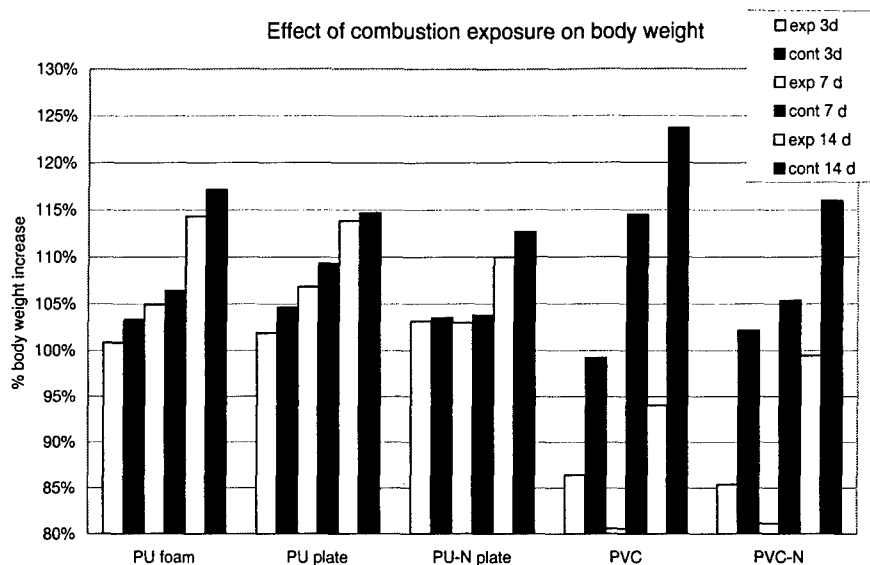


Figure 1: The effect of exposure to pyrolysis products on body weight (SEM is not shown, but was usually smaller than 3%). Only following combustion of PVC and PVC-N was a decrease in body weight observed (in comparison with parallel control animals).

3.1 Combustion of polyurethane (PUR)

3.1.1 Survival and general conditions of the animals

As can be seen in Table 1, combustion of PUR rigid foam (experiment code PU foam; LC_{50} 89 g/m³) resulted in the formation of less toxic products than PUR flexible plate (PU plate; LC_{50} 33 g/m³). Calculated on smoke formed from an amount of burnt plastic per m³ total exposure volume, the foam was approximately 2.6 times as toxic. With all PUR experiments, animals either survived or died either during or within 10 minutes of exposure. Exposed animals were usually more or less incapacitated shortly after exposure. However, they recovered quickly, and appeared healthy within several hours of exposure.

In the case of PUR flexible plate, thermolysis under oxygen-poor conditions (experiment code PU-N plate, LC_{50} 37 g/m³) appeared to be approximately as toxic as combustion under atmospheric conditions.

As can be seen in Figure 1, the body weight (3 or 7 or 14 days post-exposure) of PUR-exposed animals (series PU foam, PU plate, PU-N plate) did not (statistically significant) differ from that of the untreated control animals.

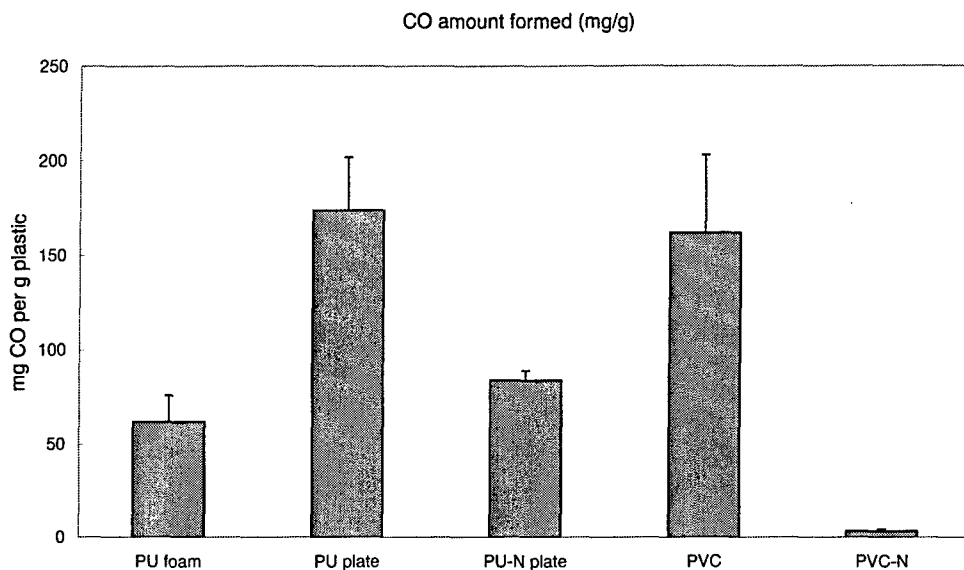


Figure 2: Emission of CO, calculated as mg CO formed per gram of plastic.

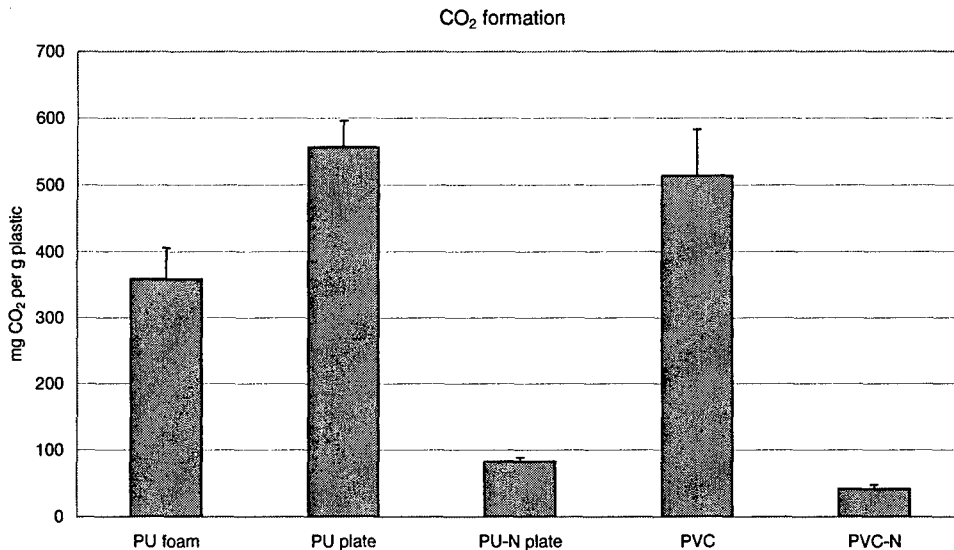


Figure 3: Emission of CO₂, calculated as mg CO₂ formed per g plastic.

3.1.2 Product formation

A number of important gaseous (or vaporous) combustion products were determined: CO, CO₂, NO₂, and HCN to relate them to the observed toxicity (Table 2). When comparing the PU foam series with the PU plate experiments, it appeared that PU foam (the least toxic of the two) produced less CO (Figure 2), less CO₂ (Figure 3) and less HCN (Figure 4). Although formed in small quantities, it is

noteworthy that reactive aldehydes as formaldehyde and acrolein were also more prominent in the PU plate combustions (data not shown).

Figure 5 shows the carboxyhaemoglobin content in the rat blood. For each series of experiments, the COHb% was calculated for the exposure equivalent to the LD₅₀. For PUR plate, the COHb is in the lethal range.

In one particular experiment, additional sampling for GC-MS was performed. Mainly nitrogen containing aromatic compounds were found, such as aminodiphenylmethane, diaminophenylmethane, benzene-isocyanate, aniline, pyridine and methylpyridine [see also Paabo and Levin, 1987].

Although nitrogen flushing did not increase the overall toxicity of combustion of PUR (compare PU plate with PU-N plate), the formation of combustion products was clearly different. In the case of the PU-N plate, much less CO (Figure 2) and hardly any CO₂ (Figure 3) were formed, but over 4 times as much HCN was found (Figure 4). Formation of HCN can be expected, as PUR contains isocyanate groups.

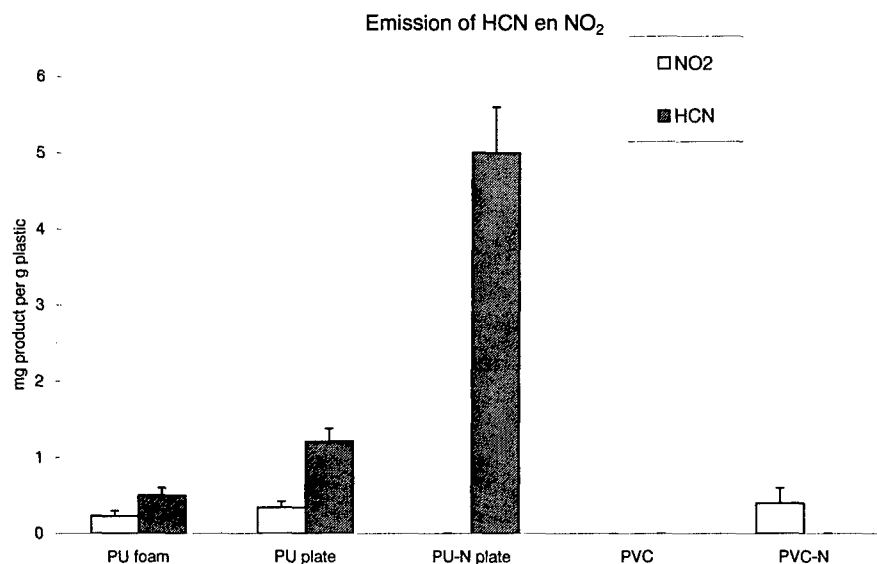


Figure 4: Emission of NO₂ and HCN, calculated as mg NO₂ or HCN formed per g plastic.

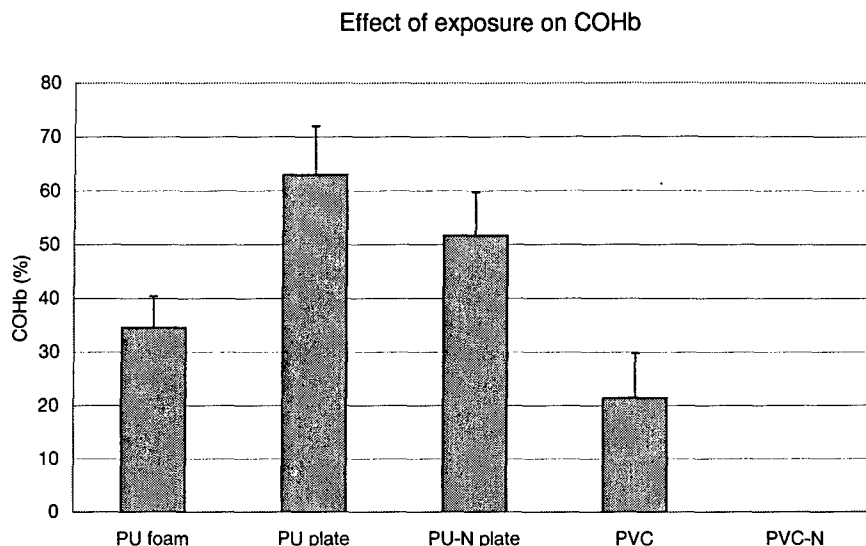


Figure 5: Effect of smoke exposure on blood carboxyhaemoglobin content.

3.1.3 Lung function measurements

The effect of exposure on respiratory frequency and respiratory minute volume was determined. The measurements were performed before and 5 minutes after exposure to the smoke. To facilitate comparison of several series of experiments, Figure 6 shows the averaged respiratory frequency for those experiments in which the highest non-lethal amount of plastic was combusted, as well as the amount causing 50% death (signals of surviving animals only). The same was done (Figure 7) for the respiratory minute volume (RMV). Between the PUR combustion experiments, no striking differences were seen: in all cases there was a rapid and vast decrease in both RF and RMV. The differences between the signals obtained in the experiments with the highest non-lethal concentrations and those obtained in the 50% survival experiments are surprisingly small.

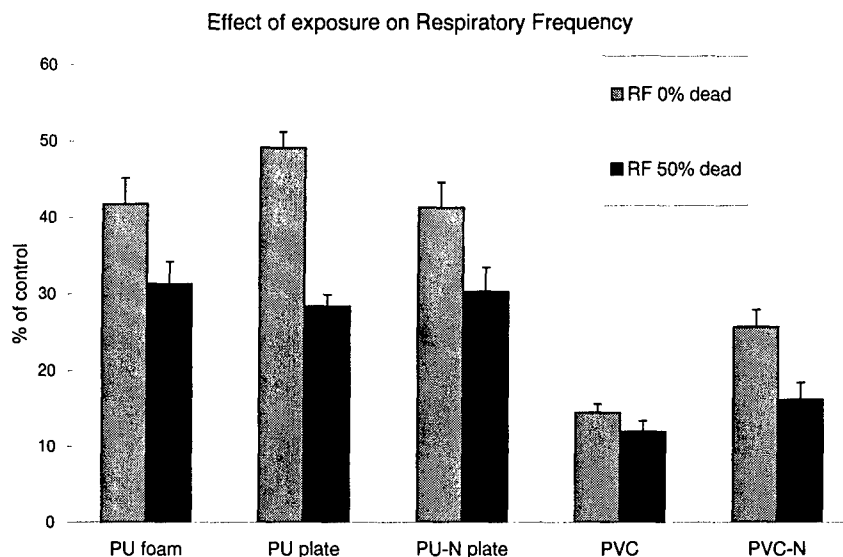


Figure 6: *Effect of smoke exposure on respiratory frequency (RF). For each plastic, the results of the experiments with the highest non-lethal amounts and with the amount corresponding with the LD₅₀ are shown.*

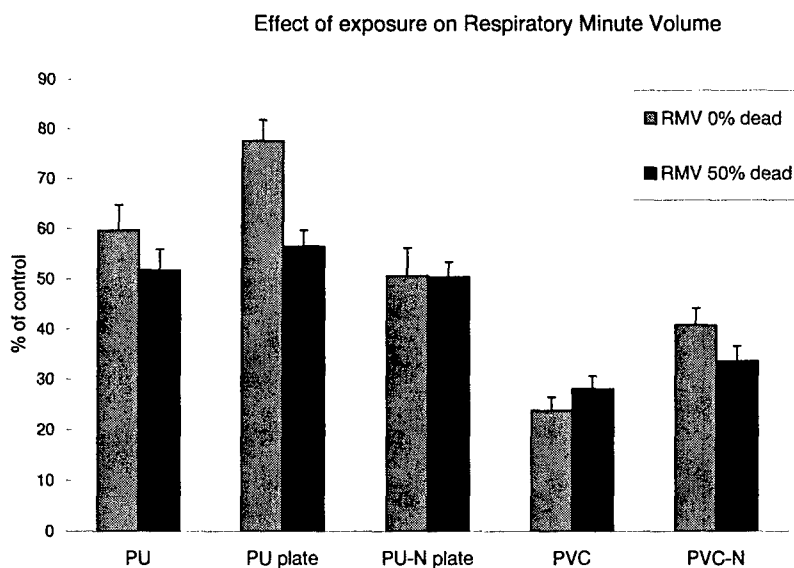


Figure 7: *Effect of smoke exposure on respiratory minute volume (RMV). For each plastic, the results of the experiments with the highest non-lethal amounts and with the amount corresponding with the LD₅₀ are shown.*

3.1.4 Lung wet weight

As can be seen in Figure 8, exposure to none of the polyurethane samples resulted in a statistically significant effect on the lung-wet weight, as measured 14 days after exposure.

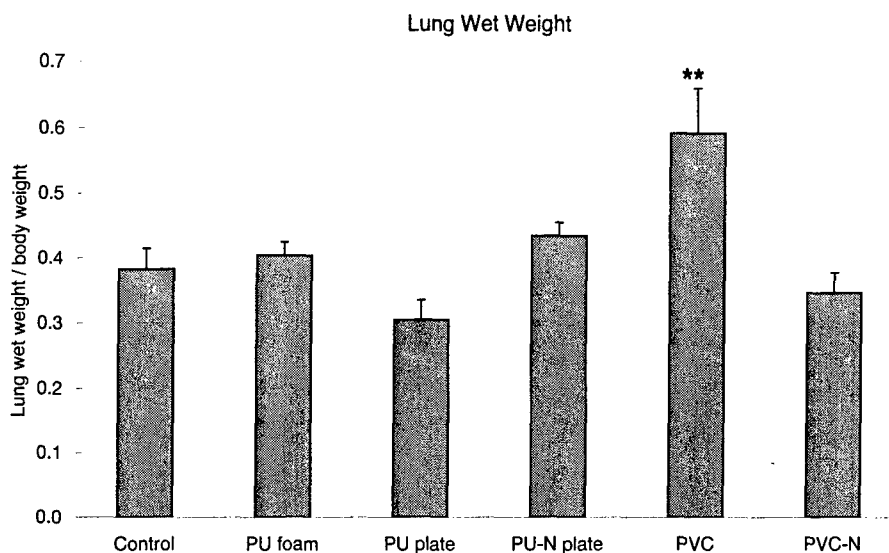


Figure 8: The effect of exposure to smoke products on lung wet weight. Only in the case of PVC a small but statistically significant increase of the lung wet weight was found.

3.1.5 Histopathology

In none of the rats from the PU foam, PU-plate or PU-N plate series, were any manifest pathological aberrations on light-microscopic level found in the lungs or the nose tissue.

3.2 Combustion of PVC

3.2.1 Survival and general condition of the animals

As was the case with PUR, the toxicity of the combustion products of PVC formed under oxygen-poor conditions was increased. The LC_{50} under atmospheric conditions (PVC) was 43 g/m^3 ; thermolysis after nitrogen-flushing resulted in an LC_{50} of 26 g/m^3 (Table 1). In both the PVC and PVC-N experimental series, the means of the times to death of the animals were much longer than in the PUR series. Most animals died between 10 and 24 h after exposure. Some rats died after several days. Only in the higher dosage experiments did a few rats die within 1 h of exposure. As can be seen in Figure 1, the animals from the PVC and PVC-N groups suffered from substantial weight loss, amounting to 35% compared to control animals 3 days after exposure. After 14 days, the relative weight loss decreased somewhat.

3.2.2 Product formation

As was expected, combustion under oxygen-poor conditions (PVC-N) resulted in very low concentrations of oxygen-containing products: CO (Table 2; Figure 2) and CO₂ (Figure 3). No increase of COHb was found in PVC-N-exposed rats (Figure 5). With PVC, the CO emission (162 mg/g) was almost as high as that of the PU plate series (174 mg/g, Fig. 2). However, the CO concentration at the (calculated) LD₅₀ combustion amount was less: 5800 ppm versus 7300 in the case of the PU plate. This was in agreement with the COHb% of 21%, which is well below lethal levels (Figure 5).

A very important combustion product of polyvinylchloride is hydrogen chloride (HCl); both in the PVC and PVC-N series; the HCl emission amounted to approximately 200 mg/g (20 mass %). Apparently, the absence of oxygen in the PVC-N series did not influence the HCl emission.

In one particular experiment, additional sampling for GC-MS was performed. Aromatic compounds such as naphtalene, phenanthrene, benzene, xylene, chlorobenzene and benzylchloride were found, all in small quantities (µg; not shown).

Table 2: Measured concentration of some toxic gases at the respective LD₅₀ amounts of each plastic divided by the (literature) LC₅₀ (15 min) values of those gases; thus 100% means exposure to 1 times the LC₅₀.

	CO	HCN	NO ₂	HCl
PU foam	101	50	4	-
PU plate	104	23	6	-
PU-N plate	36	66	-	-
PVC	83	-	-	130
PVC-N	14	-	-	76

Table 3: Results specified for each individual combustion experiment.

Experiment code LC ₅₀ (g/m ³)	Experiment no.	Amount burnt (g)	Number of deaths (N= 6)
PU foam 89	A.1	8.1	0
	A.2	10.2	1
	A.3	12.4	2
	A.4	15.1	0
	A.5	16.5	5
	A.6	22.5	6
PU plate 33	B.1	3.8	0
	B.2	5.2	1
	B.3	5.3	5
	B.4	5.8	6
PU-N plate 37	C.1	2.9	0
	C.2	4.0	1
	C.3	5.0	1
	C.4	6.0	3
	C.5	7.0	6
PVC 43	D.1	2.2	0
	D.2	3.4	2
	D.3	6.1	3
	D.4	7.0	3
	D.5	9.1	4
	D.6	14.3	5
PVC-N 26	E.1	1.9	0
	E.2	2.5	1
	E.3	3.6	3
	E.4	5.4	4
	E.5	6.3	5

3.2.3 Lung function measurements

No gross difference was seen in the lung function of rats from the PVC and PVC-N experiments. Both RF and RMV of PVC and PVC-N experiments were decreased to a larger extent than those of all PUR experiments (Figures 6 and 7).

3.2.4 Lung wet weight

The relative lung wet weight was determined by dividing the lung wet weight by the body weight. The relative lung wet weight of rats exposed to burnt PVC was significantly increased (0.591 ± 0.067) compared with the control animals (0.383 ± 0.032) and with PVC-N-exposed animals (0.346 ± 0.031): $p < 0.01$ (Figure 8).

3.2.5 Histopathology

In the PVC experiments, with lower (sublethal) doses (2.2; 3.4 g), mild effects were observed in the rat lungs: multifocal bronchio-alveolar hyperplasia (meaning: increased number of lung tissue cells in several areas of the lower airways), multifocal perivascular lymphocytic infiltration (meaning: presence of inflammatory

cells located near many blood vessels) and increased macrophage infiltration. At higher doses (6.1 g; 7.0 g), macrophages were pigmented, and pigmented bronchial lining was observed (animals surviving 14 days).

In the noses (mainly level I, the frontal side of the nose), mild dysplasia (meaning: aberrations in cell type) was seen in the lower dosed groups. With increasing amounts of burnt PVC, (focal) squamous metaplasia (meaning aberrant epithelium cells), epithelial necrosis and chronic osteomyelitis were observed. These findings, all in animals sacrificed 14 days after exposure, were most prominent in the level I area, but were also seen in level II (located deeper in the nose). All aberrations were present in respiratory, transitional and olfactory cell types.

In some of the animals that died due to PVC exposure, epithelial necrosis was found. In addition, intraluminal exsudate was found, frequently containing soot.

4 Discussion

In this and earlier reports [Busker et al., 1994 and 1997], the development and validation of a toxicological test for combustion products are described. The validation of the combustion toxicity test was achieved by demonstrating that the test could be applied to a range of comparative studies. A combustion toxicity test should primarily yield criteria to compare the hazard of a given material in a direct sense with other materials. In addition, it should yield data which allow comparison with literature data and which allow reference to existing regulations. Currently, the effective regulations on toxicity of combustion products are scarce and of low substantiality. The U.S. Navy regulations, described in NES 713, are in fact a set of test protocols. These protocols are primarily aimed at comparative combustion toxicity testing, like the test described in this paper.

To effectuate the validation process, four comparative paradigms (Table 4) were formulated, aimed at demonstrating the potential of the experimental set-up.

- 1 Comparison of plastics of comparable chemical composition but differing physical appearance.
- 2 Comparison of combustion under different atmospheric conditions. In many fires, oxygen supply is or becomes limited, therefore a combustion toxicity test must be performed under differing oxygen levels. In this case we chose combustions under the realistic extremes of 20% and 0% O₂.
- 3 Comparison of a range of chemically different materials, in this case: polyurethane versus polyvinylchloride.
- 4 Comparison with literature data. Literature data were collected from similar or differently designed combustion toxicity tests.

Table 4: Survey of experiments relating to the questions to be answered.

Issue	Description	Experiment series dealing with the given issue
1	Differing physical appearance	PU foam vs PU-plate
2	Variation of atmospheric conditions	PU plate versus PU-N plate PVC versus PVC-N
3	Different components	PVC versus PU foam/PU plate PVC-N versus PU-N plate
4	Comparison with literature data	All

- 1 The experiments addressing this question were the comparison between PU plate (polyurethane flexible plate) and PU foam (polyurethane rigid foam; Table 4). A relatively large difference was found in overall toxicity (lethality). However, in both cases the underlying toxicology appeared similar: in both cases, all animals either died immediately or survived. Respiratory frequency and minute volume decreased to an equally large extent, but the rats recovered fully within a day. All animals had high COHb levels, corresponding with the CO concentrations found. The CO concentration at the amount of PU foam yielding the LC₅₀ of the smoke mixture, was 7100 ppm. Following combus-

tion of PU plate this amounted to 7300 ppm. The LC_{50} of CO in rats is 7000 ppm at an exposure duration of 15 min [Kimmerle, 1974]. This indicates that the lethal effects are mostly due to CO intoxication [Busker et al., 1994] and that the difference between PU plate and PU foam is merely caused by the difference in CO emission per g plastic.

- 2 In this study no significant difference was found in the LC_{50} values of PU plate versus PU-N plate. Under the normal oxygen concentration (20%), much CO is formed from PU. A CO concentration of 104% of the CO LC_{50} is reached after combustion of sufficient PU to kill 50% of the animals. Under oxygen-poor conditions (PU-N), much less CO is formed, corresponding with only 36% of the CO LC_{50} . In this case, other toxic products play a more prominent role. The HCN dose, found after combustion of the LC_{50} yielding amount of PU-N plate, was 66% of the HCN LC_{50} . With PU plate this was only 23%.

The greater toxicity of PVC-N versus PVC cannot be explained simply by looking at the most common products. Much less CO was formed (from 14% of the LC_{50} compared with 83%). The concentration of HCl at the LC_{50} concentration was 130% of the its LC_{50} for PVC, whereas it was only 76% for PVC-N. The relative HCl formation was the same (199 vs 205 mg/g). This indicates that other unknown products contribute to the toxicity of PVC-N. This observation motivates a more broadened approach of the combustion toxicity issue, with more attention to by-products [Sarofim and Suk, 1994] and to the role of soot, to which components may be adsorbed.

- 3 Comparison of the toxicity of combustion products of different chemical compositions is of course somewhat arbitrary. The important issue is that the toxicity test is suitable to compare a variety of materials, as had already been demonstrated in an earlier study [Busker et al., 1997].
- 4 As far as comparison is possible, our toxicity data are in agreement with literature data (Table 5). Although the experimental set-up of methods such as the University of Pittsburgh test, the NBS test and the DIN 53436 is quite different, the overall results are of the same order of magnitude. Our method is compliant with the Pittsburgh University test as far as the set-up is concerned. It generates results that are largely in line with any of the tests used so far.

Alarie [1985] and Clarke and Hirschler [1991] provided lists of criteria and measurements required for adequate testing. These lists included aspects such as sufficiently high temperature, sufficient oxygen, flaming and non-flaming conditions, and sufficient oven capacity. It can be concluded that the TNO Prins Maurits Laboratory (TNO-PML) method for determination of toxicity of pyrolysis products of plastics is in agreement with these criteria. Possibly important exceptions are continuous monitoring of some determinant gases and the possibility of gradual

increase in temperature. We are currently developing equipment to simultaneously monitor CO, HCN and NO_x. Time-programmed temperature increase is an already built-in feature [Busker et al., 1997].

Determination of mental incapacitation by the smoke has not (yet) been incorporated. Use of in vitro toxicity testing techniques in this field is scarce, but should receive more attention. One important validation criterion is extremely difficult to approach. This involves comparison of small-scale test results with large-scale fires. A possible future development may be to expose animals to smoke mixtures obtained from larger scale combustions.

An aspect which is inherent to animal experimentation is the extrapolation of data to the human situation. From reviewing of incapacitating effects of smoke gases, both with rats and with non-human primates, it has been concluded that rats appear to be sensitive to approximately the same range of dose, as are hazardous to man [Hartzell et al., 1985].

In conclusion, it can be stated that our test appears to be applicable for testing of plastics under a relevant variety of experimental conditions. The results obtained are within reasonable agreement with those obtained from existing tests.

Table 5: Comparison of the experimental results with literature data.

Plastic	Form	Method	LCt ₅₀ (g.min/m ³)	Authors	LCt ₅₀ found (g.min/m ³) (this study)
PUR	Rigid foam	UnivPitts	520	Alarie and Anderson [1979]	1241-1429
PUR	Foam	NIBS	1450-2340	Clarke and Hirschler [1991]	
PUR	Rigid foams	DIN 53436	840	Prager et al. [1994]	
PUR	Flexible foam	UnivPitts	645	Alarie and Anderson [1979]	477-512
PUR	Flexible foam	NBS	1170	Purser [1992]	
PUR	Flexible foam	NBS	810	Doe [1987]	
PUR	Flexible PUR 20% oxygen	NBS	640	Hartzell [1991]	
PUR	Flexible PUR <5% oxygen	NBS	475	Hartzell [1991]	537-573
PVC	92% homopolymer	UnivPitts	760	Alarie and Anderson [1979]	617-673
PVC	n.s.; 20% oxygen	NBS	510	Doe [1987]	(617-673)
PVC	n.s.; <5% oxygen	NBS	600	Doe [1987]	380-400

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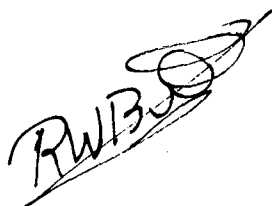
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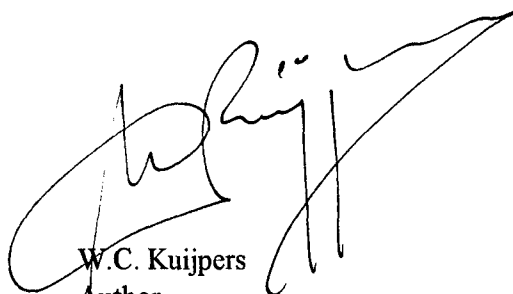
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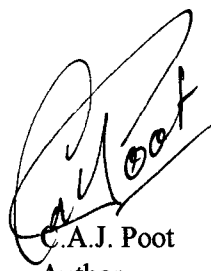
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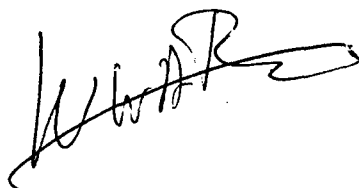
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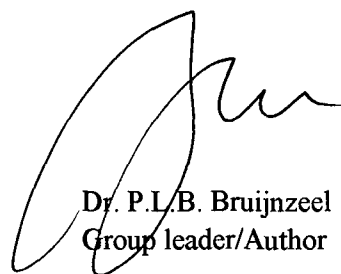
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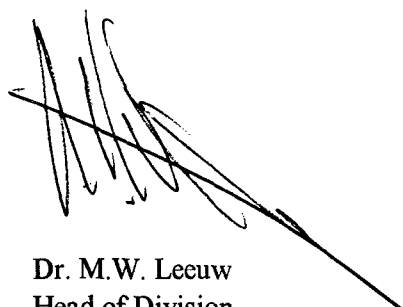
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Annex A Oven and animal exposure unit

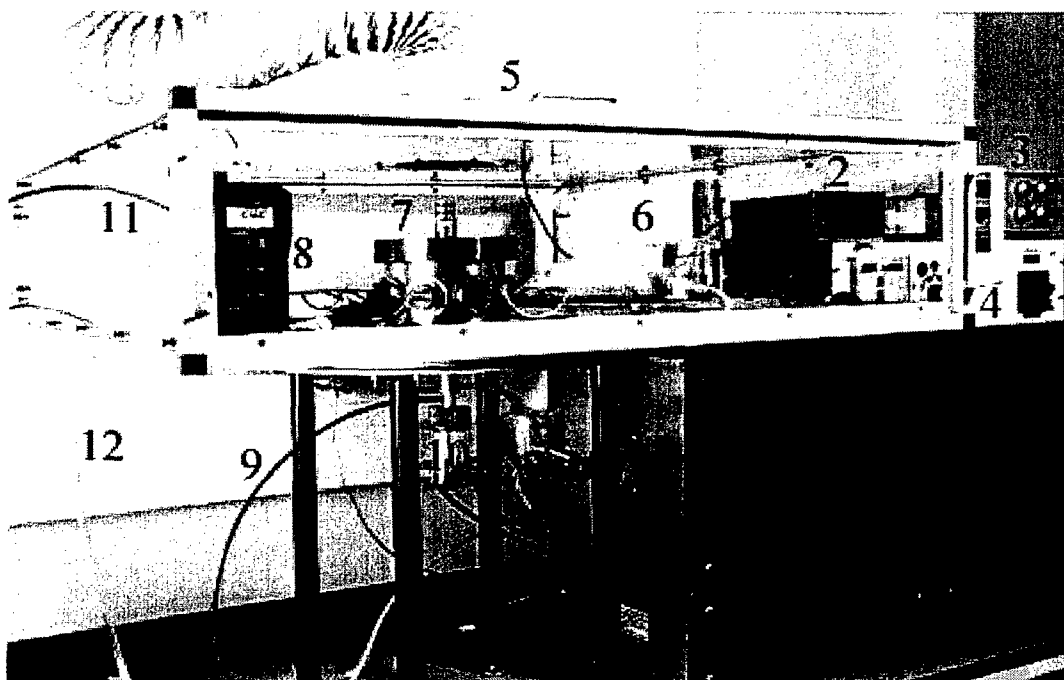


Photo A.1.

- 1 Tube furnace oven
- 2 Thermometer (smoke entering exposure unit)
- 3 Mass flow controller (flow inlets)
- 4 Oven control unit
- 5 Ventilated cabinet
- 6 Rodent Batelle tube
- 7 Jaeger nose only animal exposure unit
- 8 Thermometer (temperature at animal's nose)
- 9 Inlet of air dilution flow
- 10 Glass connectors
- 11 P3 Filter
- 12 To manometer

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15. ABSTRACT (MAXIMUM 200 WORDS (1044 BYTE)) <p>Inhalation of toxic combustion products is the major cause of death during fires. This problem is also prominent in military equipment, because of the widespread use of plastics, especially PUR and PVC. Increased knowledge of the combustion products formed and their toxicity could decrease the risks. This report describes the development and validation of a test that can be used to estimate the toxicity of the combustion products of plastics. In this test, 2-100 g of plastics are combusted, and rats are exposed to the complete smoke mixture. In addition to survival, also sublethal effects, such as respiratory depression and lung damage are investigated.</p> <p>For the validation process, a number of combustion experiments was performed, aimed at demonstrating that the test is useful to compare the toxicity of several plastics. The toxicity risk of polyurethane (PUR) could be estimated, both with PUR foam and with PUR rigid plates. The test allows the combustion to be performed under conditions with varying oxygen concentrations and temperatures. This was demonstrated using PUR and polyvinylchloride (PVC) samples. The toxic effects of PUR were mainly attributed to carbon monoxide and by hydrogen cyanide. The toxicity of PVC was partly due to the formation of carbon monoxide and by hydrogen chloride.</p> <p>Quantitatively, the results were in reasonably good agreement with literature data.</p>												
16. DESCRIPTORS <table><tr><td>Combustion products</td><td>PVC</td></tr><tr><td>Fires</td><td>Respiration</td></tr><tr><td>Military facilities</td><td>Tests</td></tr><tr><td>Plastics</td><td>Toxicity</td></tr><tr><td>Polyvinyl chloride</td><td></td></tr></table>			Combustion products	PVC	Fires	Respiration	Military facilities	Tests	Plastics	Toxicity	Polyvinyl chloride	
Combustion products	PVC											
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Military facilities	Tests											
Plastics	Toxicity											
Polyvinyl chloride												
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